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Structural Changes in Pyrolytic Graphite at Elevated Temperatures

1 DECEMBER 1963

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1 December 1963

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COMMANDER SPACE SYSTEMS DIVISION
UNITED STATES AIR FORCE
Inglewood, California

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This technical documentary report has been reviewed and is approved for publication and dissemination. The conclusions and findings contained herein do not necessarily represent an official Air Force position

For Space Systems Division
Air Force Systems Command

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ABSTRACT

Gross and unit cell dimensional changes of pyrolytic graphite have been measured as a function of heat-treatment times between 15 seconds and 10 minutes at temperatures from 2600° to 3000°C. These changes have also been measured for 4-hour heat treatments in the same temperature range. For example, growth along the basal planes and contraction in the C_o direction are 0.63 percent and 1.1 percent, respectively, for a 90-second heat treatment at 3000°C. No incubation period for these changes has been noted above 2600°C. The effects of these changes in rocket nozzle and reentry configurations are discussed.

ACKNOWLEDGMENT

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FIGURES

I. INTRODUCTION

The high ablation efficiency and high temperature strength of graphitic materials make them desirable as heat shield material for reentry vehicles. Specifically, pyrolytic graphite possesses a high degree of anisotropy in thermal conductivity that makes it an excellent conductor of heat along the surface of the vehicle as well as an excellent thermal insulator in the direction normal to its surface. Its rate of mass loss during ballistic reentry is predicted to be significantly lower than that of other types of graphite. With respect to rocket nozzle applications pyrolytic graphite offers improved erosion resistance relative to other types of graphite.

In the past, the internal stresses that resulted in fracture and delamination prevented the extensive use of pyrolytic graphite in these applications. However, after recent studies of this problem, manufacturers have developed fabrication techniques that appear to provide a solution to this problem.

Another problem that warrants investigation results from the proposed use of pyrolytic graphite in heat shields and nozzles in the sublimation region, that is, at temperatures near $3600^{\circ}C$. When subjected to temperatures in excess of the deposition temperature (2000° to $2250^{\circ}C$), structural changes occur. During the course of other studies several investigators have noted that these changes affect both the X-ray parameters and the physical dimensions. Kotlensky and Martens[1] indicate rapid structural changes above $2700^{\circ}C$; and Bragg and Packer[2] report measurable changes in 10 minutes at temperatures as low as $2400^{\circ}C$. However, structural change data are not currently available for advanced reentry and nozzle applications that involve times of considerably less than 10 minutes.

This report presents the results of a study that was undertaken to characterize the gross dimensional and microstructural changes in pyrolytic graphite; emphasis is on the short-term, high-temperature data. Such data

are essential for design of components to be used above the deposition temperature.
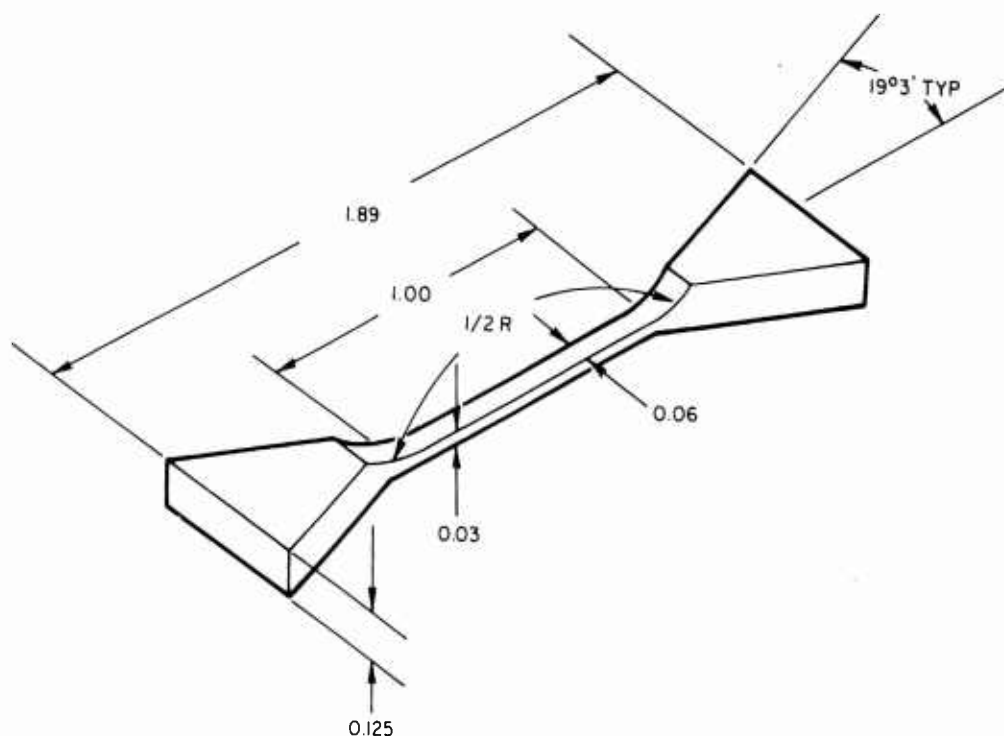
Fig. 1. Configuration of Pyrolytic Graphite Specimens Used for
Pulse Studies

One-eighth-inch, cubic specimens were heated 4 hours at temperatures
from 2000° to 3000°C to determine the effect of annealing on gross dimen-
sions and the C_o spacing. All X-ray measurements were made at room
temperature with a General Electric XRD-5 diffractometer using nickel
filtered radiation from a copper target tube operated at 50 kV and 16 mA.
An 0.4 deg MR beam slit and 0.2 deg detector slit were used throughout
the study.

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II. EXPERIMENTAL PROCEDURE

A. SPECIMENS

The material used for the thermal expansion studies was a 1/4-inch-thick plate of pyrolytic graphite.[*] This plate was formed at $2150^{\circ}C \pm 25^{\circ}$. Specimens consisted of 1/4-inch cubes. Specimens for the long term and pulse annealing studies were prepared from a 1/8-inch-thick central zone of a 3/4-inch-thick block obtained from the same source. This block was formed at the above temperature with a deposition time of 200 hours. Assuming a linear deposition rate, this zone had been annealed at $2150^{\circ}C$ for approximately 100 hours during subsequent deposition. The C_o spacing for this material varied from 6.84 to 6.86Å from the initial to the terminal deposition surfaces, respectively. The C_o spacing for the specimens was 6.852Å. Specimen configuration for the long-term studies was a 1/8-inch cube. Specimens for the pulse studies, shown in Fig. 1, were machined so that the basal planes of the graphite were parallel to the major surface. This orientation permitted study of the 002 X-ray reflections in situ.

B. LONG-TERM ANNEALING

A series of 1/4-inch-cubic specimens were heated in a thermal expansion furnace similar to that previously described.[3] Thermal expansion measurements were made parallel and normal to the basal planes in the temperature range from 1000° to $3000^{\circ}C$. An average heating rate of $10^{\circ}C/minute$ was maintained during the heating cycle. Dimensional changes were determined by measuring with a Gaertner telemicroscope the displacement of fiducial grooves cut in the edges of the cubes. The filar eyepiece of this instrument can be read to 5×10^{-5} inches over a range of 0.2 inch.

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[*]Fabricated by the High Temperature Materials Company, Boston, Mass.

C.   PULSE ANNEALING FURNACE

A special furnace was developed for pulse heating graphite to temperatures up to 3000°C in 3 seconds. This furnace, utilized for both the dimensional and the X-ray studies, is shown in Fig. 2. The specimen was clamped in two watercooled chucks, one of which is electrically insulated from the horizontally adjustable base. The cooling water outlet tubing, insulated from the base with cast epoxy, conducts electrical current to the right specimen clamp. Flexible braid permits clamp movement during the heating cycle. Electrical insulation for this clamp is provided by a teflon dovetail insert. The pyrex covers, used to contain the inert gas atmosphere, have a vent in the top for continuous flow of gas. A prism mounted on the cover is used for temperature measurement. The cover used for X-ray diffraction measurements has a 180 deg window of 0.0035-inch-thick nickel foil. This foil has a three-fold function: It is transparent to copper $K\alpha$ X-radiation; it serves as a copper $K\beta$ filter, and thereby eliminates the need for an external filter; and it retains the argon inert atmosphere. The second feature, in effect, eliminates the loss in intensity resulting from the interposition of a beryllium foil window in the X-ray beam. The cover used for the basal plane growth measurements has a flat pyrex window that provides a distortion-free view of the sample.

The center sections of the specimens were self-heated with current supplied by a 10-volt, 200-amp transformer, and temperatures were varied by adjusting an autotransformer in the primary circuit. Pulse durations were controlled by a clock timer. Since the time required for the specimens to reach 3000°C from room temperature was approximately 3 seconds, this constant was added to the desired time interval on the timer. The specimens also cooled below the deposition temperature in less than one second. Times at temperature are estimated to be correct within 1 second.

D.   PULSE TECHNIQUE TEMPERATURE MEASUREMENTS

When pyrolytic graphite specimens are directly heated, the surface temperatures, as read by an optical pyrometer, vary appreciably with

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PRISM

GAS VENT

MOVABLE BRASS
SPECIMEN BLOCK

TEFLON INSERT

SPECIMEN CLAMP

ADJUSTABLE
STAGE — BRASS

GE SPECTROGONIOMETER
BASE

X-RAY ALIGNMENT
SCREW

FLEXIBLE
TYGON TUBING

AC ELECTRICAL
CONNECTION

AC ELECTRICAL
CONNECTION

COOLING
WATER INLET

PURGING GAS INLET
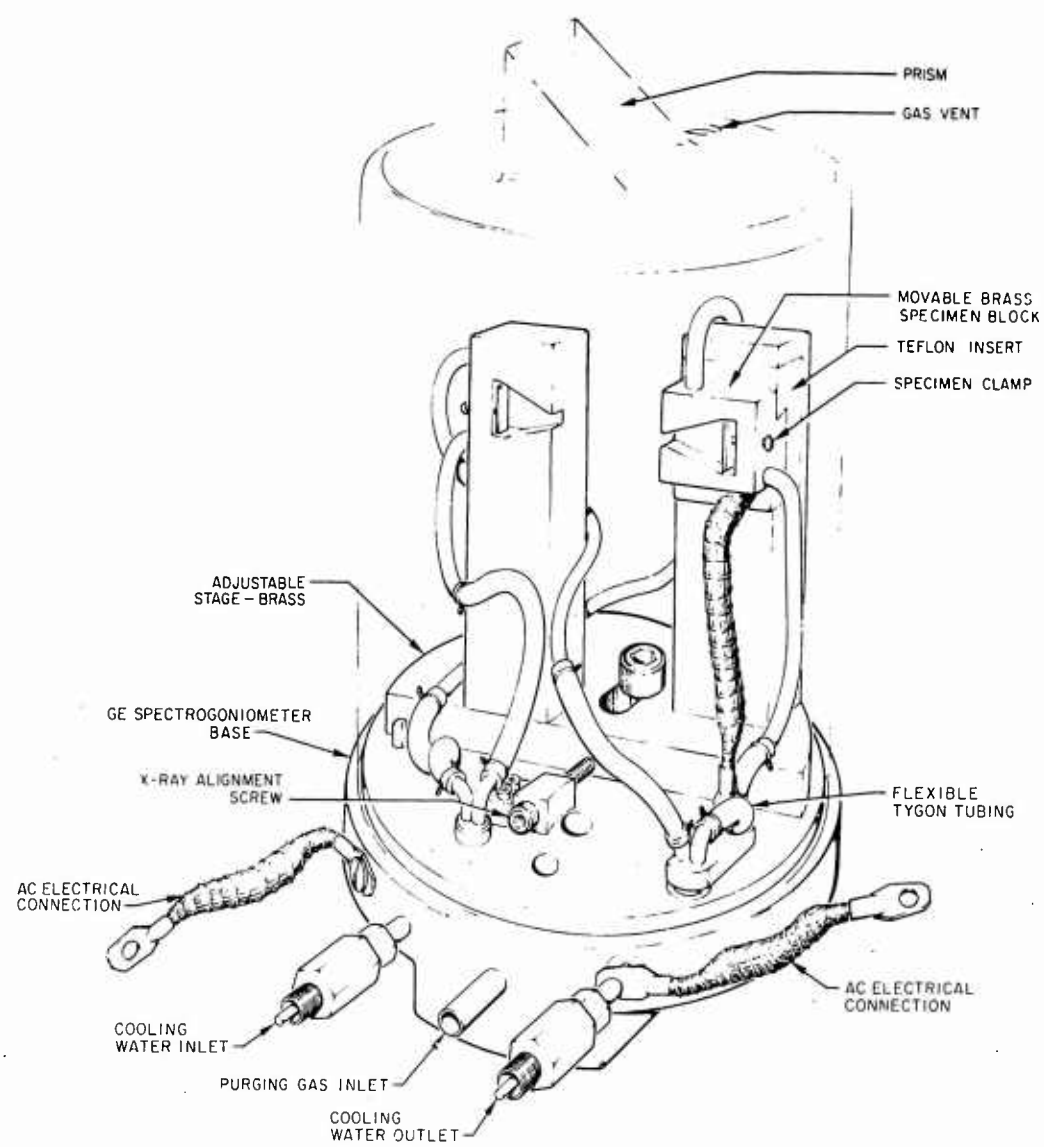
COOLING
WATER OUTLET

Fig. 2. Furnace Used for Pulse Studies

orientation, due to effects of anisotropy in thermal conductivity, as well as emissivity. The spread of low values of emissivity of the basal surface reported in the literature and the large thermal gradient existing across this surface make it difficult to determine temperature with any degree of certainty. The emissivity of a pyrolytic graphite surface normal to the basal planes, however, has recently been given[4] as 0.95, which yields a relatively small temperature correction.

Almost all radiant energy coming from the specimen passed through the pyrex glass furnace enclosure. The absorption coefficients of the flat glass window and right angle silvered prism were both determined to be 0.10. The temperatures given in this report are of the surface normal to the basal planes and include the above emissivity and absorption corrections.

Temperature profiles, along the length of the specimen, were determined up to 2600°C. Temperature drops were less than 10°C between the center of the specimen and fiducial grooves located 0.100 inch from center.

Temperatures were read by a Pyro "Micro-Optical" pyrometer that had been compared to an NBS calibrated pyrometer. The agreement between pyrometers was within 3°C up to 3000°C.

Above 2500°C a grey deposit began to form on the surface of the specimens normal to the basal planes; the rate of formation increased with temperature. This deposit consists of a loose network of graphite spherules, which tend to fill a lengthwise notch that formed simultaneously on the surface. The structure of these spherules is analogous to that of carbonblack; i.e., the basal planes of the graphite crystallites are tangential to their surface. These undoubtedly form as a result of a sublimation-condensation reaction on this surface. At temperatures above 2900°C, sublimation of graphite from this area is sufficient to form soot deposits on the furnace wall.

The low emissivity of the grey deposit and the soot on the furnace wall cause an erroneous temperature reading in about 10 seconds after the initiation of

the run. Therefore, the temperature of the specimen was determined within the first 5 seconds of the run. The grey deposit was carefully scraped from the specimen between runs, and the soot was removed. The resultant loss in cross section of the specimen did not appear to affect the power required to maintain the correct temperature of the sample during the succeeding run.

E. PULSE TECHNIQUE BASAL PLANE GROWTH MEASUREMENTS

Growth along the basal planes of pyrolytic graphite was determined by measuring, at room temperature, the residual displacement of two "V" shaped grooves cut in the specimen surface parallel to the "c" axis, spaced 0.2 inch apart. These fiducial grooves were back-illuminated by a diffuse white surface. Each data point represents an average of ten separate measurements of the location of each groove made before and after each temperature pulse. Specimen temperatures were correct to $\pm 35^{\circ}C$ across the entire test area of 0.2 inch length.

F. PULSE TECHNIQUE C_o SPACING MEASUREMENTS

The pulse furnace described in Section C was designed to be mounted directly on a General Electric XRD-5 X-ray diffractometer. Thus, pulse heating and X-ray measurements were made without removing the specimen from the furnace. Initial measurements could be made of the C_o spacing on each specimen, using standard diffractometer techniques. With a specimen in place and the X-ray source energized, the diffractometer was set to the 2θ value corresponding to the C_o spacing of that particular specimen. The X-ray adjustment screw (see Fig. 2) was then rotated until maximum, reflected intensity was obtained on the recorder. This procedure yielded the correct positioning for the specimen in the X-ray beam. Separate specimens were used for each heat treatment temperature. The choice of the 0.4 deg beam slit at a 2θ value of 23 deg resulted in an analysis area, 0.09-inch wide, at the center of the specimen. The temperature variation across this analysis area was found to be within $\pm 10^{\circ}C$ of the stated temperature.

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III.   RESULTS AND DISCUSSION

A.   THERMAL EXPANSION

Below the deposition temperature, the coefficient of thermal expansion of pyrolytic graphite falls between molded or extruded graphite and the single crystal[5] values. A typical expansion curve for the dimension parallel to the basal planes is shown in Fig. 3 for the terminal surface material. The
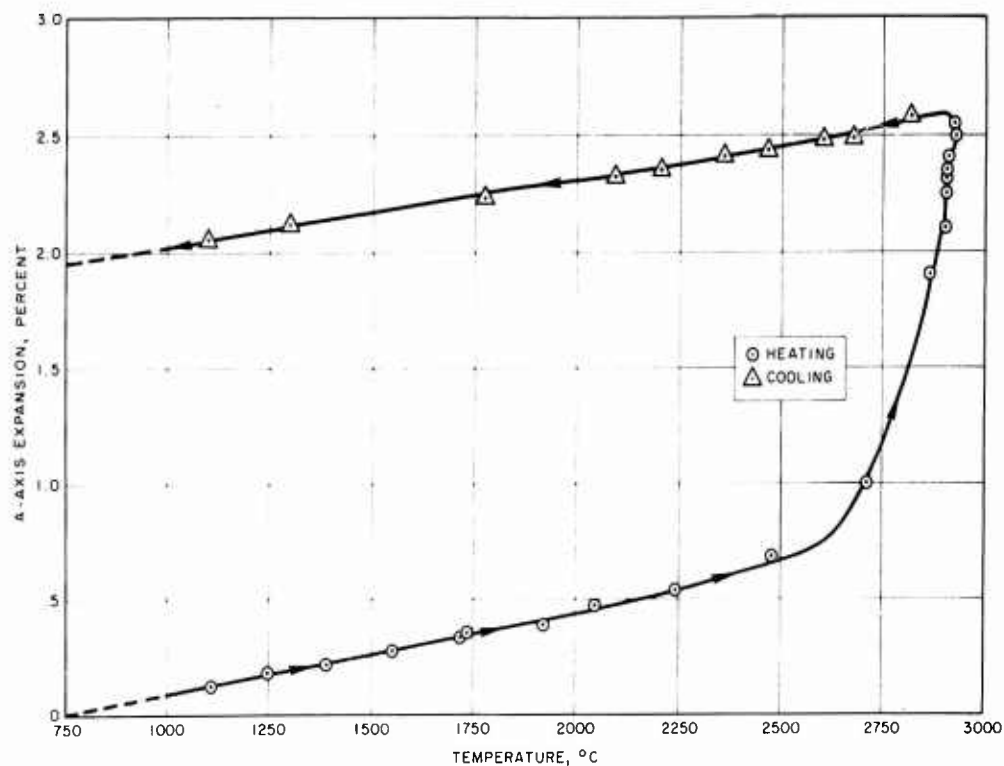

Fig. 3.   Thermal Expansion Curve for Pyrolytic Graphite, Parallel to the Basal Planes, Showing the Irreversible Expansion Above 2500°C

specimens underwent negative expansion parallel to the basal planes from room temperature to about 300°C; there was a positive expansion coefficient

above this temperature. The net expansion was zero at about 800°C. This behavior is analogous to that obtained by Nelson and Riley[6] for the A_O dimension of the graphite unit cell in this temperature range. The rate of expansion increased rapidly above 2500°C. Changes occur above 2500°C that are not reversible; and, in the above specimen, the expansion on cooling followed a curve parallel to the initial expansion curve, but it was displaced by 2 percent. This value represented a permanent elongation.

Expansion normal to the basal planes increased monotonically to about 2700°C, as shown in Fig. 4. The specimen then contracted irreversibly in
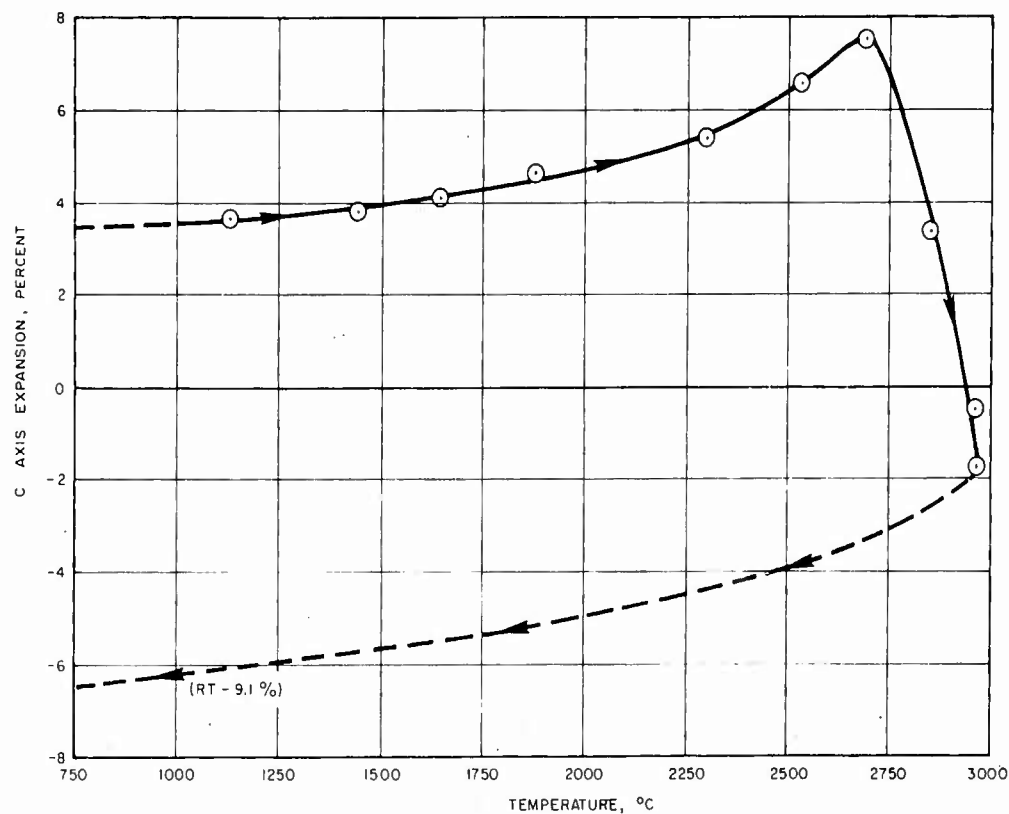

Fig. 4. Thermal Expansion Curve for Pyrolytic Graphite, Normal to the Basal Planes, Showing the Irreversible Contraction Above 2500°C

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this direction above 2700°C. Permanent contraction at room temperature was 9.1 percent.

B. EFFECTS OF LONG-TERM ANNEALING

Dimensional changes measured at room temperature on specimens parallel and normal to the basal planes that were heat treated for 4 hours at temperatures between 2000° and 3000°C are shown in Fig. 5. Contraction normal to the basal planes was noted and was found to increase in magnitude with temperature. A net change of 13.5 percent for the 3000°C run was observed. An expansion parallel to the basal plane was noted, and the magnitude of the expansion increased with temperature. A net change of 5.4 percent for the 3000°C run was observed. The results of Stover[7] are in good agreement with the present work. Kotlensky and Martens[1] have also reported contractions at 3000°C as large as 9.5 percent perpendicular to the basal planes and expansions as large as 4.1 percent parallel to the basal planes.[*] The results of these observers are shown in Fig. 5 for comparative purposes. It would appear that there is a considerable difference between the data of Kotlensky and that of Stover and the authors. This may be due to differences in material; however, it could be attributed to a time dependency of change. Indeed, time dependency has been demonstrated for a sample heated at 2900°C, as shown in Fig. 6. Stover[7] has also found a time dependency for growth at temperatures as low as 2500°C during periods of 100 minutes.

Results of room temperature measurements of C_o contraction as a function of temperature for the 4-hour heat treatment are shown in Fig. 7. The C_o spacing resulting from heat treatments at 2200°C for 4 hours is unchanged from its original value of 6.852Å. Permanent C_o contraction increases rapidly in the temperature range from 2300° to 2600°C for 4-hour heat treatments, and it assumes a constant value $C_o = 6.708\text{Å}$ at about 2800°C.

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[*] Material supplied by General Electric Company, Schenectady, New York
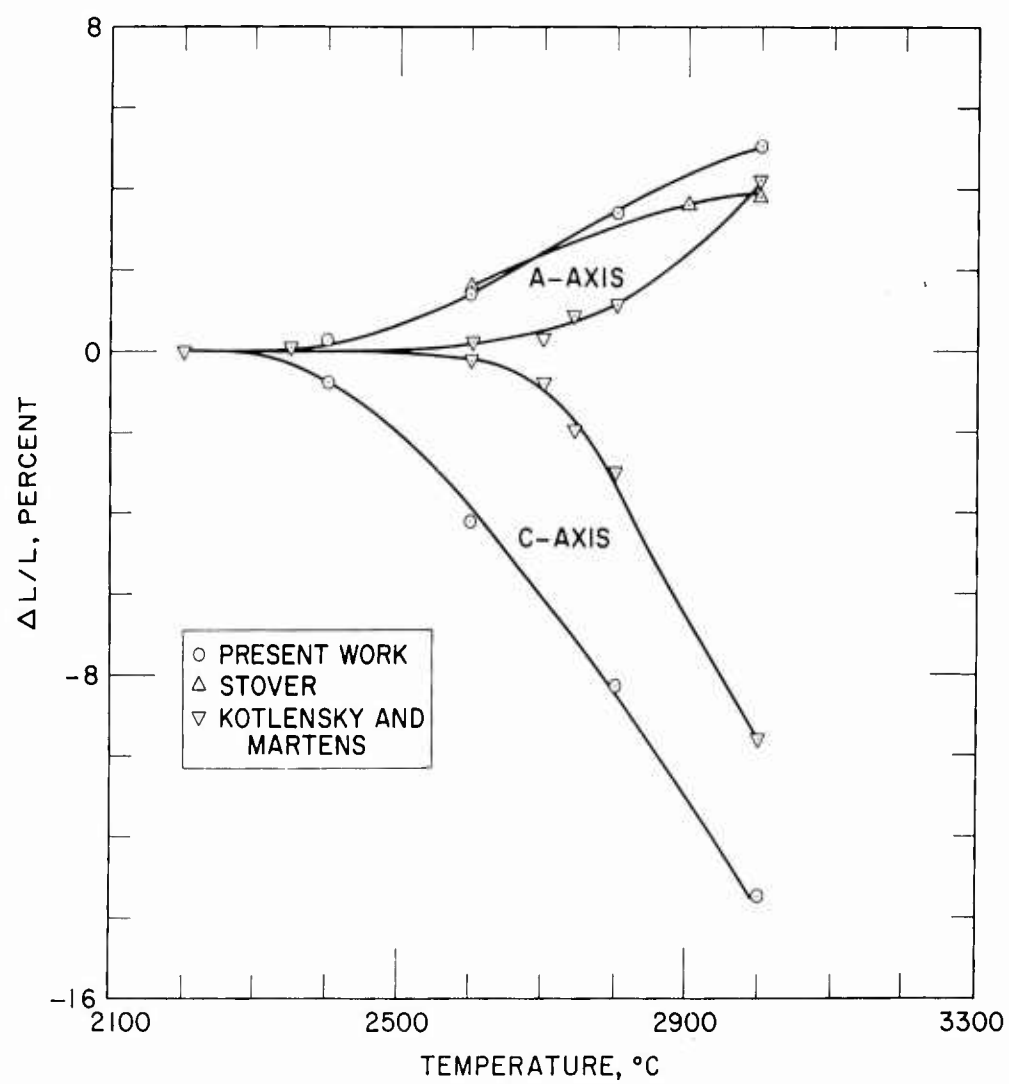
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Fig. 5.   The Irreversible, Gross Dimensional Changes in
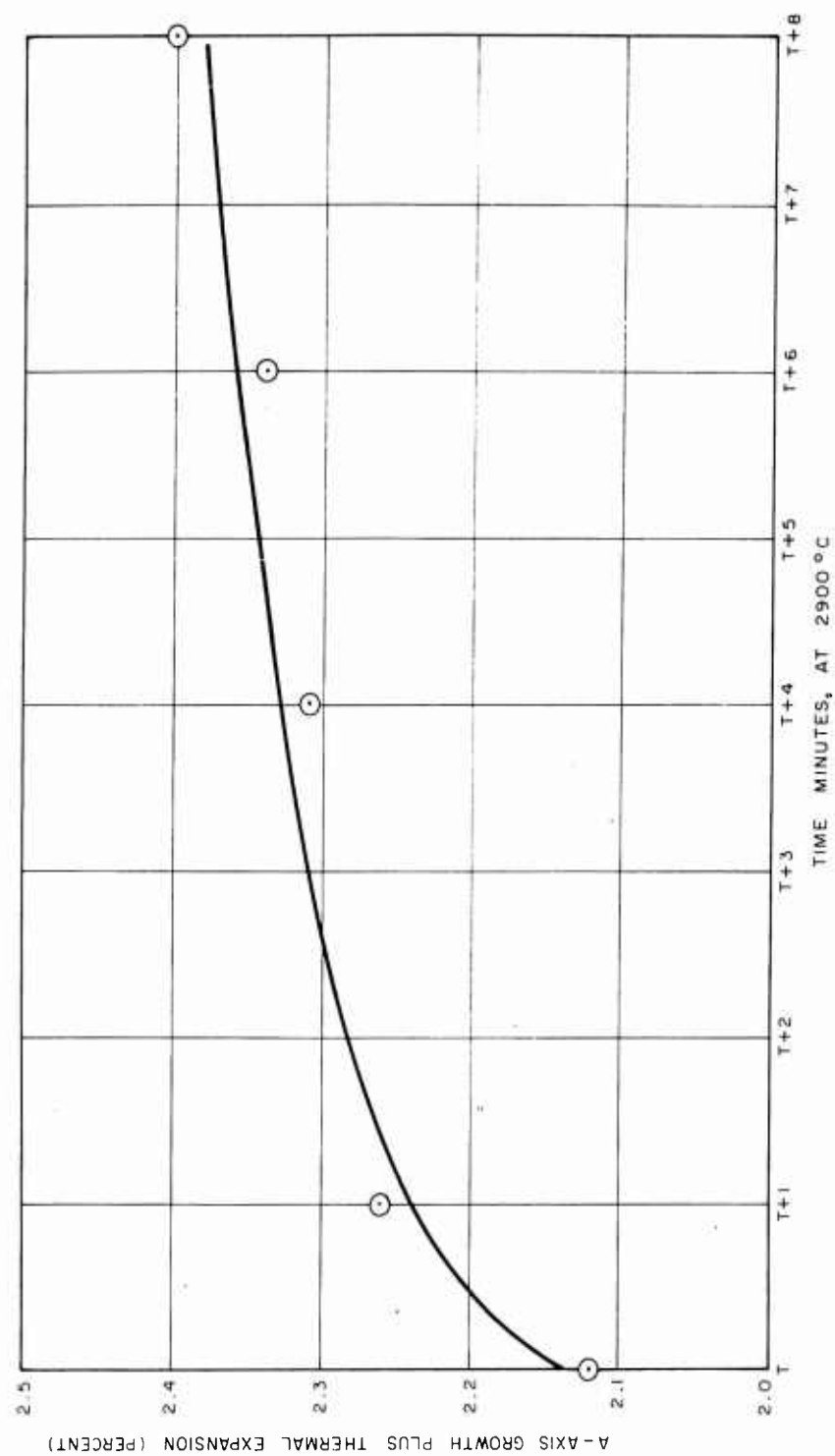Pyrolytic Graphite as a Function of Temperature

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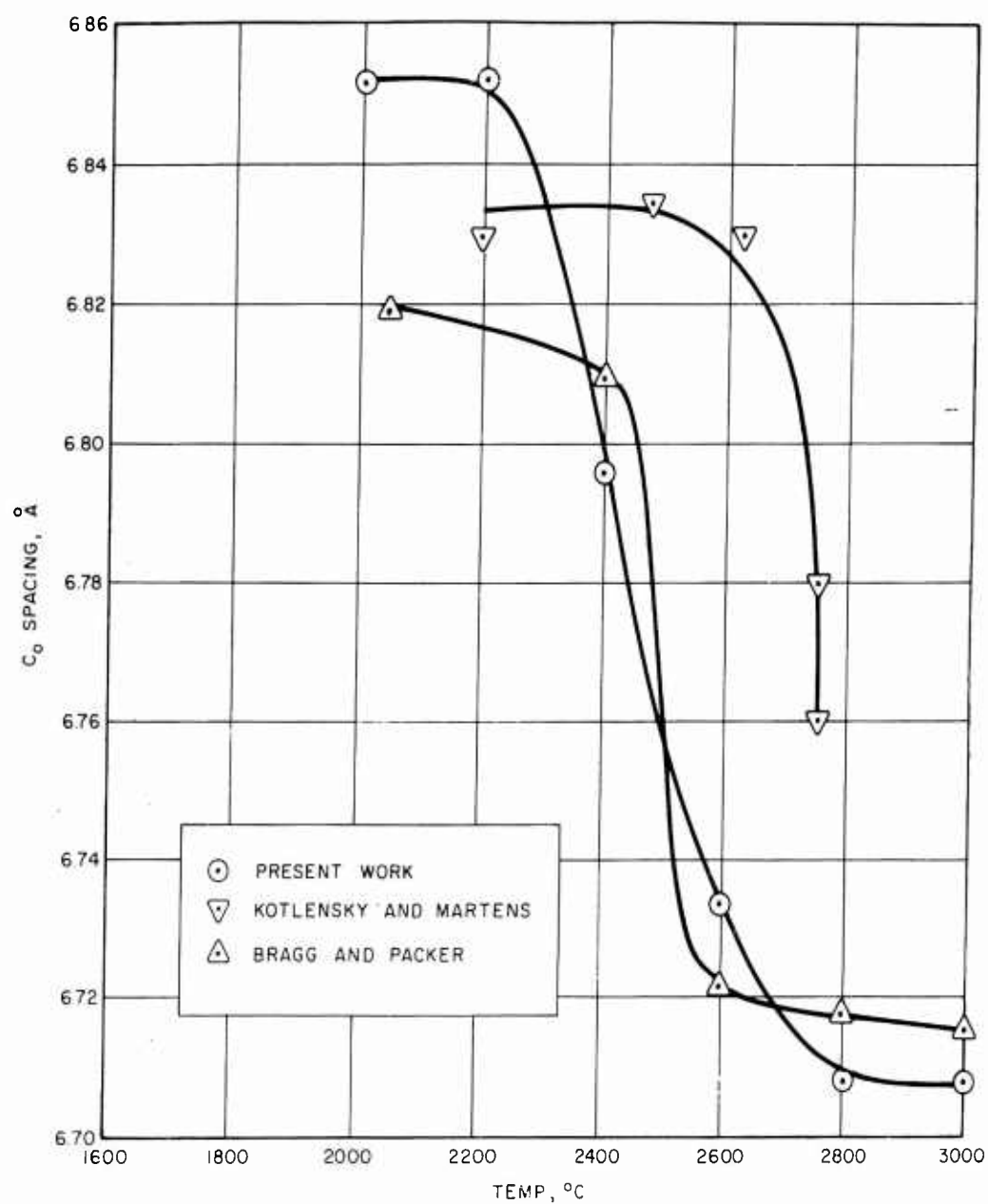Fig. 6. Time Dependency of Growth Parallel to the Basal Planes of Pyrolytic Graphite
Heated at 2900°C

Fig. 7. The Irreversible C_o Changes in Pyrolytic Graphite as a
Function of Temperature

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This value corresponds to that of the fully ordered graphite structure. These results compare favorably with data of Bragg and Packer[2] who report changes at temperatures as low as 2000°C. Furthermore, these authors found little change occurring after 10 minutes. The results of Kotlensky and Martens[1] are shown for comparison. Differences between the curves are undoubtedly due to differences in materials.

The irreversible expansion along the basal plane has been attributed by Stover[7] to layer straightening due to thermally induced internal stresses and resultant creep. The irreversible contractions normal to the basal planes are due to the layer straightening mentioned above and to ordering in the graphite crystallites, as demonstrated by C_o contraction. However, it may be seen from inspection of Figs. 6 and 7 that crystallite contraction accounts for only a small fraction of the over-all contraction normal to the basal planes.

C. PULSE STUDIES

Data are listed in Table 1 and depicted graphically in Fig. 8 relating the percentage growth in the direction parallel to the basal planes to time at temperature for times of less than 10 minutes. Dimensional growth above 2600°C is characterized by an initial high rate, increasing with temperature; it is followed by a gradual decrease in rate at longer times. No observable growth occurred at 2600°C for a 10-minute heat treatment. At 2800°C a growth of 0.15 percent was noted after 1 minute, while at 3000°C a growth of 0.55 percent was noted. It was necessary to use three specimens to obtain the 3000°C data. Agreement among these specimens is noteworthy.

Permanent changes in C_o spacing as a function of time at temperature are given in Table 2 and are plotted graphically in Fig. 9 for the temperature range mentioned above. The same general behavior is depicted in the curves of Figs. 8 and 9. The rates of contraction increase rapidly with temperature in the early stages of the process, then become more gradual. In the

Table 1. Percentage Growth Along Basal Plane
Versus Time at Temperature

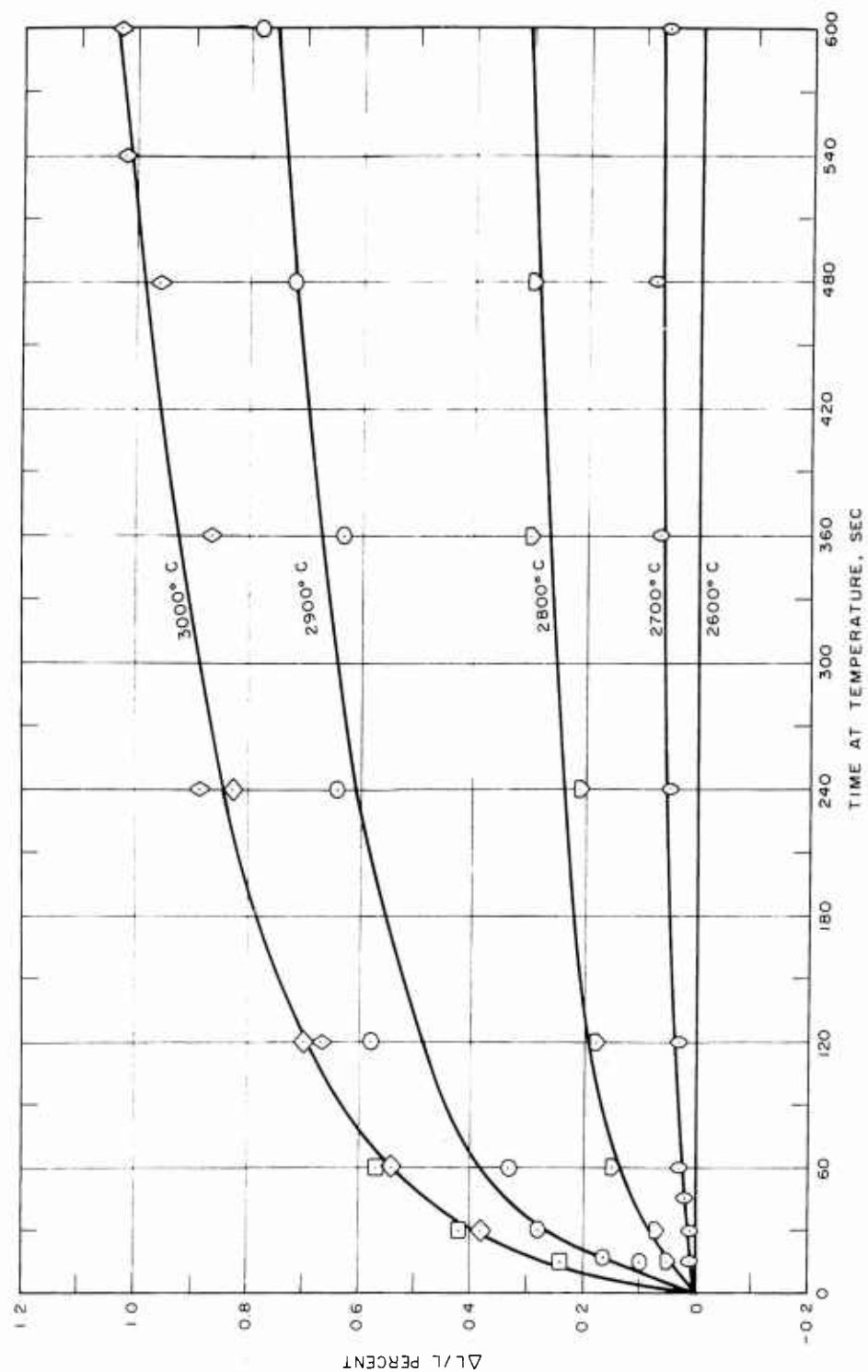| Time sec	Percentage of Growth						
	2600 $^{\circ}C$	2700 $^{\circ}C$	2800 $^{\circ}C$	2900 $^{\circ}C$	3000 $^{\circ}C$	3000 $^{\circ}C$	3000 $^{\circ}C$
15	no change	+ 0. 01	0. 05	0. 10	0. 24	0. 28	-
30	-	0. 01	0. 06	0. 28	0. 42	0. 38	-
60	-	0. 03	0. 15	0. 33	0. 57	0. 54	0. 54
120	-	0. 03	0. 18	0. 58	-	0. 70	0. 67
240	-	0. 05	0. 21	0. 64	-	0. 83	0. 89
360	-	0. 07	0. 30	0. 63	-	-	0. 87
480	-	0. 08	0. 30	0. 72	-	-	0. 96
540	-	-	-	-	-	-	1. 02
600	-	0. 06	-	0. 78	-	-	1. 03

Fig. 8. Short-term, Dimensional Changes, Parallel to the Basal Planes of Pyrolytic Graphite, as a Function of Time at Temperature
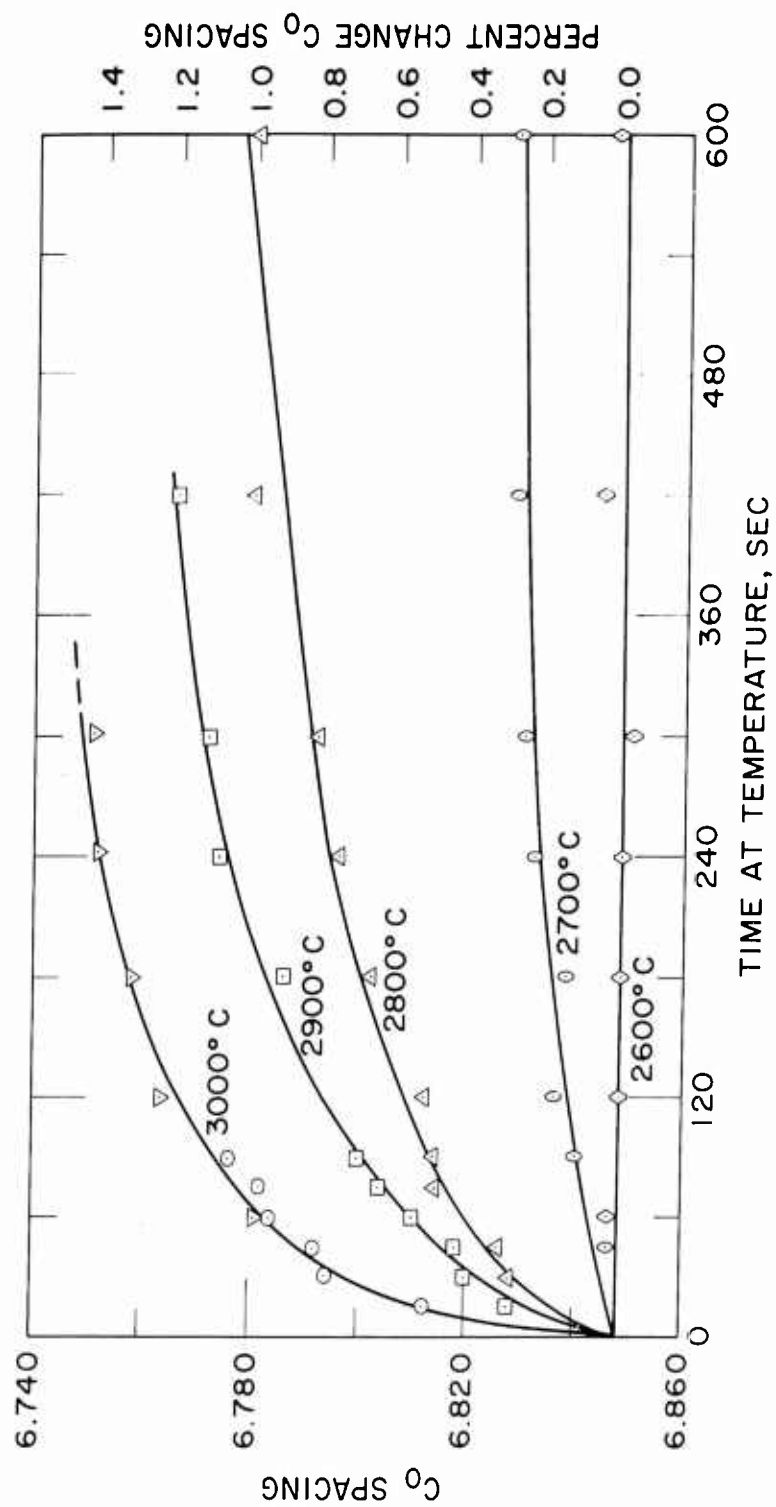
Fig. 9. Short-term C_o Changes in Pyrolytic Graphite as a Function of Time at Temperature

Table 2. C_o Spacing as a Function of Time at Temperature

Time sec	2600°C	2700°C	2800°C	2900°C	3000°C	3000°C
0	6.848	6.848	6.848	6.848	6.848	6.848
15	-	6.848	-	6.828	6.812	-
30	-	6.850	6.828	6.820	6.794	-
45	-	6.826	6.824	6.818	6.792	-
60	6.846	6.846	-	6.810	6.784	6.782
75	-	6.844	6.814	6.804	6.782	-
90	-	6.840	6.814	6.800	6.776	-
120	6.848	6.836	6.812	6.784	-	6.764
180	6.848	6.838	6.802	6.786	-	6.758
240	-	6.832	6.796	6.774	-	6.752
300	6.850	6.830	6.792	6.772	-	6.752
420	6.844	6.828	6.780	6.766	-	-
600	6.846	6.828	6.780	-	-	-
900	6.848	6.820	6.762			

short times under consideration, no limiting values for C_o spacings were observed. No incubation periods were noted above $2600^{\circ}C$ for changes in either the physical dimensions or the C_o spacing. Two specimens were used to obtain the $3000^{\circ}C$ curve; agreement was good between these two runs.

An increase in preferred orientation was inferred from the increase of X-ray peak height during the course of the runs. No quantitative determinations were made, as this behavior has been verified by others, including Stover[7] and Bragg and Packer.[2]

It is significant to note that no delamination was experienced with any specimen even though they were repeatedly cycled to high temperatures.

It should be emphasized that the long term data cannot be considered to be an extension of the pulse data, inasmuch as the specimen materials are different in the two studies. Experiments are currently in process to permit correlation between short- and long-term studies.

IV. SUMMARY AND CONCLUSIONS

Heat treatment of pyrolytic graphite above the deposition temperature results in gross dimensional and microstructural changes, which are summarized below.

The magnitudes of gross and unit cell structural changes caused by annealing commercially available pyrolytic graphite at temperatures between 2600° and 3000°C for 4 hours are shown in Figs. 5 and 7, respectively. A time dependency for these changes has been established.

The change in C_o is a small fraction of the total gross dimensional changes normal to the basal planes. Also, while the contractions in the C_o, as shown by the X-ray measurements, begin to occur at 2200°C, the changes in the gross dimensions do not occur until 2400°C. Thus, the C_o contraction is not a good criterion for the gross dimensional change in the "c" direction.

Gross and unit cell dimensional changes have been measured for commercially available pyrolytic graphite as a function of time for heat treatment times between 15 seconds and 10 minutes at temperatures from 2600° to 3000°C. (Refer to Figs. 8 and 9, respectively.) No incubation times have been observed above 2600°C.

These structural changes are accompanied by an increase in preferred orientation of the graphite crystallites. This suggests an additional problem: The effect of increased preferred orientation is to reduce the critical shear stress along a pyrolytic graphite surface parallel to the deposition mandrel. A reduction in the critical shear stress on these surfaces could lead to spallation and eventual failure of the mission. A study of the critical shear stress as a function of preferred orientation at elevated temperature will be undertaken to evaluate the seriousness of this phenomenon.

It is not clear at present just how these structural changes will limit the use of pyrolytic graphite in rocket nozzle and reentry applications. However, changes of this nature must be taken into account when the use of pyrolytic graphite is considered for applications above its depositional temperature.

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